

## COAL CLEANING: A PRE-COMBUSTION AIR TOXICS CONTROL OPTION

David J. Akers, Robert L. Dospoy, and Clifford E. Raleigh, Jr.  
CQ Inc.  
One Quality Center  
Homer City, PA 15748

Barbara Toole-O'Neil  
Electric Power Research Institute  
Palo Alto, CA 94303

**Keywords:** Coal Cleaning; Air Toxics Control; Trace Element Reduction

### INTRODUCTION

A number of elements and their compounds commonly found in coal are identified by the Clean Air Act (CAA) of 1990 as among 189 hazardous air pollutants (HAPs). These elements include: antimony, arsenic, beryllium, cadmium, chromium, cobalt, lead, manganese, mercury, nickel, and selenium. In addition to these specific elements, radionuclides are also listed as HAPs; these too are known to occur naturally in some coals. Finally, fluorine, in the form of hydrofluoric acid, is listed. The CAA mandates a study of utility air emissions. This study, to be performed by the United States Environmental Protection Agency (EPA), is expected to be presented to Congress by November 1995. In addition, EPA is required by law to perform a health risk assessment and to recommend new air toxic regulations, if necessary, to protect human health. Furthermore, the legislation requires separate studies of mercury emissions, deposition, and health effects. In order to make estimates of power plant HAP emissions, EPA requires information on the HAP concentrations in as-fired coal (i.e., as burned by utilities).

### PUBLIC SOURCES OF COAL TRACE ELEMENT DATA

Starting in 1973 and continuing through the present, the United States Geological Survey (USGS) has collected and analyzed thousands of channel and core samples of coal for various quality parameters. The measurement of trace element content was part of this geochemical study. Channel and core samples are sometimes taken of the entire height of a coal seam, including interbedded rock and minerals (partings). In such cases, they represent in-place coal, which is similar to as-mined coal without the roof or floor rock sometimes extracted along with the coal during mining (out-of-seam dilution). USGS sampling protocol is to treat partings under ten centimeters thick as part of the coal seam, while those greater than ten centimeters thick are sampled separately unless they are normally extracted with the coal during mining. Partings are sometimes removed separately in surface mining, but in underground mining, they are always extracted with the coal. Therefore, USGS samples taken in underground mines normally represent in-place coal, while those taken from surface mines may or may not represent in-place coal.

Currently, no comprehensive trace element database is available to government and industry other than the database developed by the USGS. EPA is constrained by the absence of other comprehensive data sources and may use the USGS database for the emissions estimates necessary to perform the health risk assessments required by the Clean Air Act Amendments even though the available analyses are for in-place coal and not as-fired coal. This is a concern because, as shown in Table 1, about 77 percent of eastern and midwestern as-mined coal is cleaned before it is burned. In some cases, the primary effect of coal cleaning is to remove out-of-seam dilution; however, partings may also be removed during cleaning along with fracture filling mineral matter. Recent studies have demonstrated that coal cleaning can also reduce the concentration of most trace elements (Akers and Dospoy, 1993 and DeVito et al., 1993). Since the coal samples in the USGS represent as-mined or in-place coal, the trace element data in the USGS database on many of the eastern and midwestern coals will be higher than as-fired data because most of these coals are cleaned before combustion. Health risk assessments based on the existing USGS coal database will, therefore, tend to overestimate the risk of burning eastern and midwestern coal.

### THE CURRENT PROJECT

CQ Inc., under funding by the Electric Power Research Institute, developed an approach that can be used to make coal samples in the USGS database more representative of as-fired rather than in-place coal. This paper presents a description of this approach, which involved the development of regression equations and algorithms for each of 11 trace elements. These equations and algorithms are used to predict the amount of a trace element in as-fired coal given the trace element analyses of channel and core samples in the USGS database. The

paper also presents discussion of the accuracy of the projections and provides an example of how the algorithms are being used.

The final part of this project, currently in progress, is to select those coals in the USGS database that exceed the typical as-fired ash content for the seam and county in which they were mined. For each USGS sample that exceeds the typical ash content, the appropriate algorithm will be applied to predict the trace element concentration of the core or channel sample assuming the coal had been cleaned to the typical ash content. At the conclusion of the project, a modified version of the USGS database will be available for estimating power plant emissions of HAPs.

#### **MATHEMATICAL MODELING AND REGRESSION ANALYSES**

Mathematical equations can often be developed to describe the relationships between input and output parameters of a system. In some cases, equations that are derived from theoretical or generally accepted cause-and-effect relationships can be used for modeling reactions to changes in measurable parameters. This is sometimes referred to as mechanistic or fundamental modeling. However, when theoretical knowledge about the relationships between inputs and outputs of a system is lacking, empirically-derived equations may still be developed to describe variable relations in a system.

A common method of empirical modeling is statistical correlation. Correlation, which involves the development of equations to relate results to system effects, can be used to analyze process data, describe its tendencies, and evaluate the intensity of associations among process parameters. A disadvantage with this modeling method is that the existence of a correlation does not mean that the system outputs are necessarily causally related to the input variables used to build the model. A measure of high correlation indicates only that the random variation of the data can be mathematically explained and that a specific tendency or behavior within the data is identified. However, when used correctly, statistical correlation can be an effective and reliable modeling method.

The primary operation involved in statistical correlation is regression analysis. Regression involves fitting linear or nonlinear mathematical equations to data sets in order to describe changes in dependent variables resulting from changes in independent parameters. In the case of linear regression, this is typically referred to as "least-squares" line fitting. In addition, regression is sometimes completed in stages to eliminate variables that are found to be mathematically and statistically unimportant; this is known as step-wise regression.

In order to develop equations that can predict the content of selected trace elements in clean coal after commercial-scale conventional coal cleaning, regression analyses were performed to relate various raw coal quality parameters and cleaning performance data to the trace element reduction. The data used for this work was collected from several sources: CQ Inc. has a database that includes ten commercial-scale coal cleaning tests; Consolidation Coal Company (CONSOL) has published information on trace element reductions in eight commercial cleaning plants (DeVito et al., 1993); and Bituminous Coal Research (BCR) has published trace element data for six commercial plants (Ford and Price, 1982). Finally, Southern Company Services, Inc. (SCS) gathered data on two commercial-scale cleaning tests during a project funded by DOE and EPRI. The final report for the SCS work has been prepared and supplied to EPA by DOE. Altogether, trace element removal data from 26 commercial-scale cleaning tests using coal mined east of the Mississippi River were located. Sufficient information was located to allow development of equations for the following elements: arsenic, beryllium, cadmium, chromium, cobalt, fluorine, lead, manganese, mercury, nickel, and selenium.

Multi-parameter, backward elimination regression analyses and statistical analysis of variance were conducted to develop equation models for each of 11 trace elements. For each system, trace element reductions from the commercial-scale coal cleaning tests and their respective raw coal quality parameters and coal cleaning performance results were gathered and stored into a database file. Various mathematical transformations (square root, logarithmic, and negative inverse) of the original data were also generated and included within this file. Regression of data transformations provided a means to ensure that both linear and non-linear correlation possibilities were examined. These data sets were then input to Minitab™, a computer software statistics package, for backward elimination regression. Information and output from Minitab includes statistics on summary of fit (the applicability and hardness of the equation to describe the variances in the data), analysis of variance, and parameter estimates. All of the equations developed contained ash reduction as a major predictive parameter. Three of the equations also included a total sulfur reduction predictor, while several equations included one or more raw coal analyses in addition to ash reduction.

#### DATA SCATTER AND MODELING ACCURACY

The primary method used to evaluate regression equation accuracy was to evaluate the comparative fit of measured trace element reductions versus calculated trace element reductions. An example of this method of accuracy check is shown in the figure. In these types of graphs, the dotted line represents an exact correlation between the measured and predicted reductions. That is, if data appear on this line, the equation produced exactly the same value that was measured for a particular coal cleaning test. Similarly, values that plot away from this line indicate that the equation predicted trace element values greater than or less than the actual measured values. Therefore, equation accuracy can be determined by the distance individual values are away from this line. In this example, the graphic suggests that the equation developed for fluorine is accurate, though some points are a significant distance from the line. Some portion of this data scatter is likely caused by sampling or analytical error, but other explanations must also be considered.

Lack of fit may also be caused by differences in the mode of occurrence of these trace elements in raw coal and differences of response to a variety of coal cleaning operations. The mode of occurrence of an element is the physical form and location in which the element is found within a raw coal. In general, trace elements can be found within either the organic portion of a coal or within the mineral matter that is associated with a raw coal. When trace elements are associated with mineral matter or exist as discrete mineral particles, physical coal cleaning methods can be used to remove much of the mineral matter and trace elements from a raw coal. For example, mercury has been reported to occur in coal in a variety of modes: it can be found in pyrite, in epigenetic pyrite, and in sulfides other than pyrite as well as organically bound within coal (Finkelman, 1980). Any organically-bound mercury that may occur in coal cannot be removed by physical coal cleaning technologies, while epigenetic pyrite is often coarse grained and readily removable. Thus, if mercury is organically-bound, concentrations will increase with cleaning; if it is contained in coarse-grained mineral matter, it will be reduced by cleaning with quantities dependent upon the cleaning devices employed, method of operation, and coal characteristics.

Local geologic environment during and after coal formation can also affect the mode of occurrence of a trace element. As a result, mode of occurrence may vary between coal basins or even within a single basin. Because trace element mode of occurrence may vary with location, it is reasonable to expect such a change to be reflected in the geographic location of the coal samples used. An indication of possible impacts based on geographic location is shown in the fluorine data. The figure shows that for the Pennsylvania coals, measured fluorine reductions are always equal to or lower than their corresponding predicted values. For the Alabama coal samples, this situation is reversed--measured fluorine reductions are always equal to or higher than the predicted values. This indicates that the mode of occurrence of fluorine in Pennsylvania coals may inhibit the effectiveness of coal cleaning to remove this trace element. Conversely, the mode of occurrence of fluorine in Alabama coals may help make its removal easier. Unfortunately, when the data used in this study were grouped by state of origin or by coal basin, the number of commercial-scale tests became too small to allow a statistical assessment of the impact of geographic location.

The level of trace element reduction obtained during coal cleaning can also be affected by the different techniques and technologies utilized to remove ash-forming and sulfur-bearing minerals. However, as with location differences, this could not be adequately addressed in this study because of insufficient data. To illustrate this point, consider that most of the known mineral forms of mercury in coal are sulfides, which are typically dense, finely-sized minerals. When liberated from raw coal by crushing or grinding, sulfides can be easily removed by cleaning devices that depend on the differences in density between coal and mineral matter--this is the most common method of coal cleaning. Examples of density-based cleaning devices, which have a wide range of applicability and varying degrees of coal-mineral matter separation performance, include heavy-media cyclones and baths, jigs, and concentrating spirals. Other devices such as froth flotation or agglomeration units clean coal based on the differences in surface properties between the coal and mineral matter. The surface characteristics of many sulfides and coal are sometimes very similar, though, which makes sulfide removal using surface-based methods difficult at times.

#### AS-FIRED COAL QUALITY DATA

In order to use the regression equations to adjust the USGS channel or core sample data to an as-fired basis, it is first necessary to estimate the ash and sulfur content of a target clean coal. The quality of clean coal produced from coal cleaning plants is primarily driven by raw coal characteristics and market price and specifications. Because raw coal characteristics vary by region and seam and because utility fuel quality demands can vary from region to region, a wide spectrum of clean coal qualities are produced for the utility market. In order to

develop clean coal quality targets that are applicable to specific samples in the USGS database, both raw coal characteristics and local market specifications must be examined.

Within a very limited geographical area (e.g., a county), the characteristics of an individual coal seam are reasonably uniform. In addition, most of the clean coal that is produced from a particular seam in this limited region is of similar quality, especially if much of the coal produced in the localized region is competing for fuel sales to the same electrical generating station. Thus, clean coal quality targets used in algorithms that adjust USGS as-mined or in-place coal quality data to typical as-fired quality levels must be developed for each individual seam in a given county where active mining is occurring. Several public databases and other published sources can be used in gathering the specific information needed to relate regional coal production and individual coal seam information.

#### SAMPLE ALGORITHM CALCULATION

To apply the algorithms developed during this project, the following information is necessary:

- Initial sample data (raw coal quality data or USGS channel or core data).
- Target clean coal quality.
- The calculated ash, and in some cases sulfur, reduction between the initial sample and the target quality.
- The results of applying the regression equations.
- The results of the trace element concentration calculation.

The sample calculation presented below illustrates the procedures for determining the expected nickel concentration in the cleaned Sewickley Seam coal from Pennsylvania.

#### SAMPLE DATA

Raw Ash = 32.9%; Raw Heating Value = 9,804 Btu/lb; Raw Nickel = 23.5 ppm

#### TARGET CLEAN COAL QUALITY (Assumed)

Typical As-fired Sewickley Seam Coal, Greene County, PA

Ash = 12.0% and Heating Value = 13,300 Btu/lb

#### REDUCTION CALCULATION

Ash reduction is calculated by the following equation:

$$\text{Ash Reduction} = \frac{\frac{\text{Raw Coal Ash Content}}{\text{Raw Coal Heating Value}} - \frac{\text{Clean Coal Ash Content}}{\text{Clean Coal Heating Value}}}{\frac{\text{Raw Coal Ash Content}}{\text{Raw Coal Heating Value}}} \times 100$$

$$\text{Ash Reduction} = \frac{\frac{32.9}{9,804} - \frac{12.0}{13,300}}{\frac{32.9}{9,804}} \times 100 = 73.11\%$$

#### APPLICATION OF THE REGRESSION EQUATIONS

In this example, the equation for nickel reduction is used:

$$\text{Nickel Reduction} = \frac{1}{[-0.0867 + (0.0368 \times \text{Log (Ash Reduction)})]} - \frac{1}{[-0.0867 + (0.0368 \times \text{Log (73.11)})]} = 55.23\%$$

#### TRACE ELEMENT CONCENTRATION CALCULATION

Once the calculated nickel reduction is determined, the next step is to determine the clean coal nickel concentration using available raw coal data for heating value and nickel concentration and the target clean coal heating value.

$$\text{Nickel Reduction} = \frac{\frac{\text{Raw Coal Nickel Content}}{\text{Raw Coal Heating Value}} - \frac{\text{Clean Coal Nickel Content}}{\text{Clean Coal Heating Value}}}{\frac{\text{Raw Coal Nickel Content}}{\text{Raw Coal Heating Value}}} \times 100$$

$$55.23 = \frac{\frac{23.5}{9,804} - \frac{\text{Clean Coal Nickel Content}}{13,300}}{\frac{23.5}{9,804}} \times 100$$

$$\text{Clean Coal Nickel Content} = \left[ \left( \frac{55.23}{100} \right) \times \frac{23.5}{9,804} \right] + \frac{23.5}{9,804} \times 13,300 = 14.27 \text{ ppm}$$

Table 2 shows the results of applying this algorithm to adjust the trace element concentration of raw Sewickley Seam coal to an as-fired quality using each of the equations developed for the 11 trace elements. The table also provides a measure of the accuracy of this approach, with differences in predicted versus actual concentrations averaging about 20 percent.

#### **SUMMARY**

In order to make more representative estimates of power plant HAP emissions and to perform the health risk assessments required by the Clean Air Act Amendments, EPA requires information on the HAP concentrations in as-fired coal (i.e., as burned by utilities). Currently, the USGS coal database is the only comprehensive source for information on the trace element concentration of coals that is openly available to EPA. Unfortunately, USGS samples taken from many eastern and midwestern underground and surface mines represent in-place or as-mined coal, but not as-fired coal, which is often cleaned before it is burned. To address this problem, equations and algorithms were developed to convert trace element analyses in the USGS database from an in-place to an as-fired basis. This work has provided one means for modifying the USGS database so that it can be used to estimate power plant emissions of HAPs. The study also provides a tool to estimate the impacts of using conventional or advanced coal cleaning techniques to reduce the concentration of trace elements in coals burned by utilities.

#### **REFERENCES**

Akers, D. and Dospooy, R., "An Overview of the Use of Coal Cleaning to Reduce Air Toxics," Minerals and Metallurgical Processing, Published by The Society for Mining, Metallurgy, and Exploration, Littleton, CO, Vol. 10, No. 3, pp 124-127, August 1993.

DeVito, M., L. Rosendale, and V. Conrad, "Comparison of Trace Element Contents of Raw and Clean Commercial Coals," Presented at the DOE Workshop on Trace Elements in Coal-Fired Power Systems," Scottsdale, AZ, April 1993.

Finkelman, R., Modes of Occurrence of Trace Elements in Coal, PhD Dissertation, University of Maryland, Published by University Microfilms International, Ann Arbor, MI, 1980.

Ford, C. and A. Price, "Evaluation of the Effects of Coal Cleaning on Fugitive Elements: Final Report, Phase III," DOE/EV/04427-62, July 1982.

**Table 1. Extent of Coal Cleaning by State.** Includes metallurgical, steam, and industrial coal.

| State         | Estimated Raw Coal Mined<br>(Million Tons/Year) | Estimated Tonnage Cleaned<br>(Wt %) |
|---------------|---|-------------------------------------|
| Alabama       | 37.7  | 77                                  |
| Illinois      | 83.7  | 93                                  |
| Indiana       | 49.5  | 93                                  |
| Kentucky      | 215.6   | 65                                  |
| Maryland      | 4.9   | 92                                  |
| Ohio          | 46.7  | 81                                  |
| Pennsylvania  | 90.2  | 73                                  |
| Tennessee     | 7.0   | 38                                  |
| Virginia      | 62.0  | 81                                  |
| West Virginia | 223.6   | 81                                  |
| Total/Average | 821.0   | 77                                  |

Source: Coal Preparation and Solids Division, U.S. Department of Energy, Pittsburgh Energy Technology Center, Pittsburgh, PA 15236.

**Table 2. Results of an Application of Algorithms on Raw Sewickley Seam Coal**

| Trace Element | Actual Raw Coal Conc.<br>(ppm) | Actual Clean Coal Conc.<br>(ppm) | Predicted Clean Coal Conc.<br>(ppm) | Absolute % Difference<br>Predicted vs. Actual |
|---------------|--------------------------------|----------------------------------|-------------------------------------|---|
| As            | 14.40                          | 9.20                             | 8.43                                | 9.1   |
| Be            | 1.07                           | 0.98                             | 1.21                                | 19.0  |
| Cd            | 0.21                           | 0.10                             | 0.12                                | 16.7  |
| Cr            | 44.00                          | 23.60                            | 29.49                               | 20.0  |
| Co            | 8.74                           | 4.11                             | 5.66                                | 27.4  |
| F             | 226.0                          | 97.90                            | 114.42                              | 14.4  |
| Pb            | 88.80                          | 5.15                             | 45.54                               | 88.7  |
| Mn            | 206.00                         | 73.00                            | 73.19                               | 0.3   |
| Hg            | 0.18                           | 0.18                             | 0.16                                | 12.5  |
| Ni            | 23.50                          | 11.20                            | 15.26                               | 26.6  |
| Se            | 3.61                           | 2.85                             | 2.81                                | 1.4   |

**Estimation of Algorithm Accuracy. Fluorine.**

